

## Research Paper

## A HeCol cycle for upgrading the ambient heat: The dynamic verification of desorption stage

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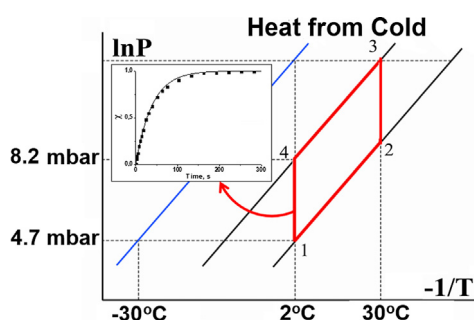
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## HIGHLIGHTS

- Methanol desorption from carbon ACM35.4 was studied under conditions of HeCol cycle.
- The desorption (regeneration) is initiated by drop of the methanol pressure at 2 °C.
- The desorption dynamics depends on the size of carbon grains and the bed thickness.
- The carbon can be quickly regenerated under unfavourable conditions of HeCol cycle.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

This paper addresses the dynamic study related to a novel adsorption cycle “Heat from Cold” (HeCol) recently proposed for upgrading the ambient heat in cold countries. In this cycle, the adsorbent is deemed to be regenerated by a drop of the adsorptive pressure, whereas the heat needed for desorption is supplied from a natural heat reservoir at a quite low temperature close to 0 °C. The aim of this study is to verify whether such unusual regeneration mode is feasible under typical conditions of the HeCol cycle. Methanol was used as an adsorptive and the activated carbon ACM35.4 - as an adsorbent.

It has been shown that such way of regeneration is certainly achievable for the working pair involved which makes the new cycle possible in principle. The methanol desorption can be completed within 5–20 min depending on the configuration of the flat adsorbent bed, namely, the size of the carbon grains and the bed thickness. The maximal specific power of this process can reach 2.4 kW kg<sup>-1</sup> that is encouraging for designing compact HeCol units.

## 1. Introduction

Adsorption heat transformation (AHT) is attracting an increasing attention due to its ability of effective conversion/storage of waste and renewable heat [1–3]. Recently, a novel AHT cycle called “Heat from Cold” (or HeCol) has been suggested for amplification of the temperature potential of the ambient heat in cold countries [4]. The HeCol cycle

consists of two isosteres and two isotherms and operates between three thermostats at low  $T_L$ , middle  $T_M$ , and high  $T_H$  temperatures (Fig. 1a). A comprehensive description of the new cycle can be found elsewhere [4].

The HeCol cycle significantly differs from a common AHT cycle which is driven by adsorbent heating up to at least 50–60 °C [5]. In cold countries during winter time, there are often no heat sources available

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### Nomenclature

$A$	slope coefficient ( $\text{kW m}^{-2}$ )
$d$	pore size (nm)
$D$	grain size (mm)
$H$	heat of evaporation ( $\text{J g}^{-1}$ )
$m$	adsorbent mass (mg)
$n$	vapour concentration ( $\text{m}^{-3}$ )
$P$	pressure (mbar)
$q$	adsorption uptake ( $\text{g g}^{-1}$ )
$S$	specific surface area ( $\text{m}^2 \text{g}^{-1}$ ), heat transfer surface ( $\text{m}^2$ )
$T$	temperature ( $^{\circ}\text{C}$ )
$t$	time (s)
$V$	pore volume ( $\text{cm}^3 \text{g}^{-1}$ )
$W$	specific power ( $\text{W kg}^{-1}$ )

### Greek symbols

$\Delta$	increment
$\chi$	dimensionless conversion degree
$\tau$	characteristic time (s)

### Subscripts

0	initial
0.7	70% conversion
2	stage 2
4	stage 4
H	high
L	low
M	middle
max	maximal

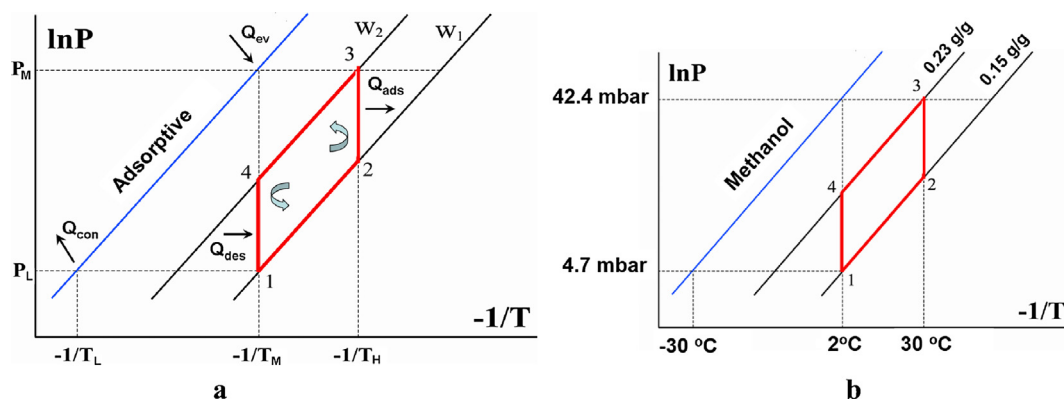


Fig. 1. P-T diagram of a 3T HeCol cycle: a – general schematics; b – the cycle studied in this work.

at this temperature level. In this case, the desorption (regeneration) can only be performed by a drop of adsorptive pressure over the adsorbent as suggested in [4]. The heat necessary for desorption is supplied to the adsorbent from a natural heat reservoir at the highest temperature available during winter. At the best, this could be underground water with  $T_M = 10\text{--}30\text{ }^{\circ}\text{C}$ . In the worst case, it is a non-freezing water from natural basins, such as river, lake, sea, ocean, at  $T_M = 0\text{--}4\text{ }^{\circ}\text{C}$ .

The thermodynamic operation of the HeCol cycle is found to be encouraging as

- the first law efficiency  $\eta_{\text{FLT}} = Q_{\text{ads}}/(Q_{\text{des}} + Q_{\text{ev}}) \approx 0.5$  is low itself. However, the heats for desorption  $Q_{\text{des}}$  and evaporation  $Q_{\text{ev}}$  are taken **for free** from an inexhaustible natural heat reservoir at  $T_M$ , whereas the useful heat  $Q_{\text{ads}}$  can have a temperature potential sufficient for heating, thus, gaining a commercial value [4];
- the theoretical second law efficiency  $\eta_{\text{SLT}}$  is rather high ( $> 0.6$ ) [4]. A practical  $\eta_{\text{SLT}}$ -value can be close to the theoretical one because the adsorbent regeneration due to a pressure drop results in smaller entropy production than a common (thermal) regeneration by the adsorbent heating accompanied by irreversible heat transfer from an external heat source [6].

Despite the promising thermodynamic issues, the implementability of the new cycle remains questionable, first of all, because the temperature of the desorption stage is rather low (commonly  $0\text{--}4\text{ }^{\circ}\text{C}$  as mentioned above). If the rate of desorption process is limited by breaking chemical bonds between adsorbate and adsorbent, the rate  $W$  is expected to be proportional to  $\exp[-E_a/(RT)]$ , where  $E_a$  is the activation energy of desorption,  $R$  is the universal gas constant, and  $T$  is the adsorbent temperature. In this case, the ratio

$$W(T_1)/W(T_2) = \exp[-E_a(T_2 - T_1)/(RT_1 T_2)] \quad (1)$$

can be estimated for the typical regeneration temperatures of the HeCol cycle ( $T_1 = T_M = 2\text{ }^{\circ}\text{C} = 275\text{ K}$ ) and that of the common AHT cycle ( $T_2 = 100\text{ }^{\circ}\text{C} = 373\text{ K}$ ). If consider methanol to be an adsorbate and assume  $E_a \geq Q_{\text{ev}} = 35\text{ kJ/mol}$ ,  $W(275\text{ K})/W(373\text{ K}) \leq 0.02$ , hence, at the lower temperature, the adsorbent regeneration dramatically slows down that can stop practical realization of the HeCol cycle. Much smaller rate reduction is expected if the desorption is limited by the Knudsen diffusion in the adsorbent pores:  $W(275\text{ K})/W(373\text{ K}) = (275\text{ K}/373\text{ K})^{0.5} = 0.85$ . All other scenarios lie within these limits.

Therefore, the aim of this work was to directly study the desorption dynamics under typical conditions of the HeCol cycle, to find out whether this stage can be performed with the rate acceptable for practical purposes. A commercial activated carbon ACM-35.4 was used as an adsorbent, and methanol as an adsorbate. This carbon is an up-to-date analogue of the famous carbon AC-35 that was widely studied as the methanol adsorbent for AHT units [7,8]. The working pair “methanol – ACM-35.4” has already been theoretically analyzed for the HeCol cycle in [6].

## 2. Identification of the desorption conditions

Equilibrium of methanol adsorption on the carbon AC-35 was earlier studied in [9]. The authors found that it cannot be described by the classic BET [10] and Langmuir [11] models. More fruitful approach is based on the Polanyi potential theory [12] that lies on the base of very popular empirical equations proposed by Dubinin [13]. This empirical approach considers the adsorption process to be similar to condensation, and the adsorbed state to behave like a liquid, that results in a

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